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# THERMAL ACCELERATION OF OZONE INTERACTION WITH GRAPHITE AND OTHER ORGANOCARBONS

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Prepared by Sandia Laboratories, Albuquerque, New Mexico 87115
and Livermore, California 94550 for the United States Atomic Energy
Commission under Contract AT (29-1)-789

OCTOBER 1975

Sandia Laboratories

SF 2900 Q(7-73)

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## ABSTRACT

Reactions of ozone with graphite and selected hydrocarbons at elevated temperatures were investigated. An energy activation curve for graphite was generated and the activation energy for graphite at the temperature range of 30°C to 180°C was determined to be 16.8 k Cal/mole. Mildly activated flux from a hybrid microcircuit soldering operation, not completely removable by solvents, and preventing reliable thermocompression bonding, may be completely removed in 5 minutes by corona discharge generated ozone in oxygen when reaction is promoted at 150°C.

Acknowledgement

The author is indebted to J. N. Sweet, 2151, for assistance with the graphite activation energy calculations and to I. E. Dunn, Jr., 2152, for assistance in setting up the ozone generating equipment and making titration measurements.

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## INTRODUCTION

Ozone is known to be highly reactive with organic materials. A high concentration of ozone, such as 6 wt% generated by corona discharge in an oxygen gas carrier was, however, in spite of its high reactivity slow in removing decomposed soldering flux at room temperature. This report documents work which demonstrated the increased reactivity of ozone on several organocarbons including graphite at temperatures above ambient to 180°C.

There was special concern for soldering flux because its complete removal by solvents is difficult. In hybrid microcircuit assembly requiring both soldering and thermocompression bonding, the thermocompression bonding process may be seriously impeded or completed bonds may be unreliable because of undetected residual soldering flux left on the hybrid circuitry prior to thermocompression bonding. Early experimental cleaning using the ozone from a mercury discharge lamp in air at room temperature resulted in effective residual flux removal. This allowed excellent thermocompression bonding results, however, long exposure times (in terms of hours) were required.

P. H. Holloway and D. W. Bushmire[1] have demonstrated the reaction of high concentrations of ozone on photoresists at ambient temperature. R. R. Sowell[2] has used the effect of ultraviolet from a mercury discharge lamp combined with the ozone produced plus oxidation by air. A. D. Bolon and C. O. Kuntz[3] also used ultraviolet depolymerization of photoresist polymers but did not experience any reactive increase at higher temperature. The oxidative effect of ozone on carbon black has been reported, but no comprehensive data is known to be available for its effect on graphite.

## PROCEDURE

The equipment used consisted of a corona discharge ozone generator, an oxygen supply, and a heat source. (See Figure 1 & 2) The ozone generator (Model 03B1-0) was a product of Ozone Research and Equipment Corporation, Phoenix, Arizona. The specially designed aluminum chamber for exposing materials to ozone reaction had an inside area about 5 cm x 10 cm and a 8.4 sq. cm cross section to oxygen and ozone (gas) flow. These materials were chosen for minimum reactivity with ozone and for durability at elevated temperatures. As may be noted in Figure 1, a Minneapolis-Honeywell temperature controller provided hot plate temperature regulation, and, in addition, a thermocouple readout meter was used for visually monitoring chamber

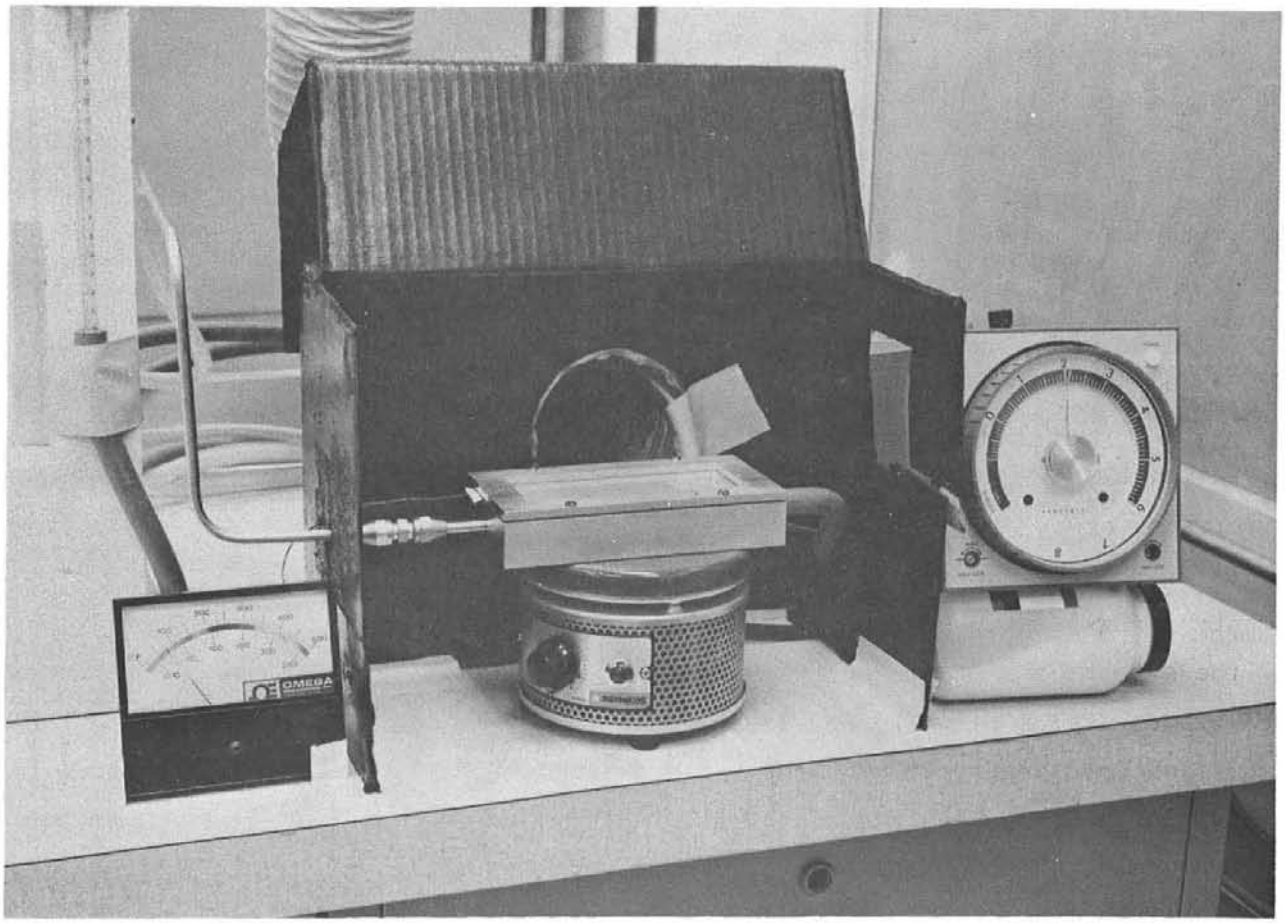


Figure 1. Aluminum Chamber and Monitoring Equipment

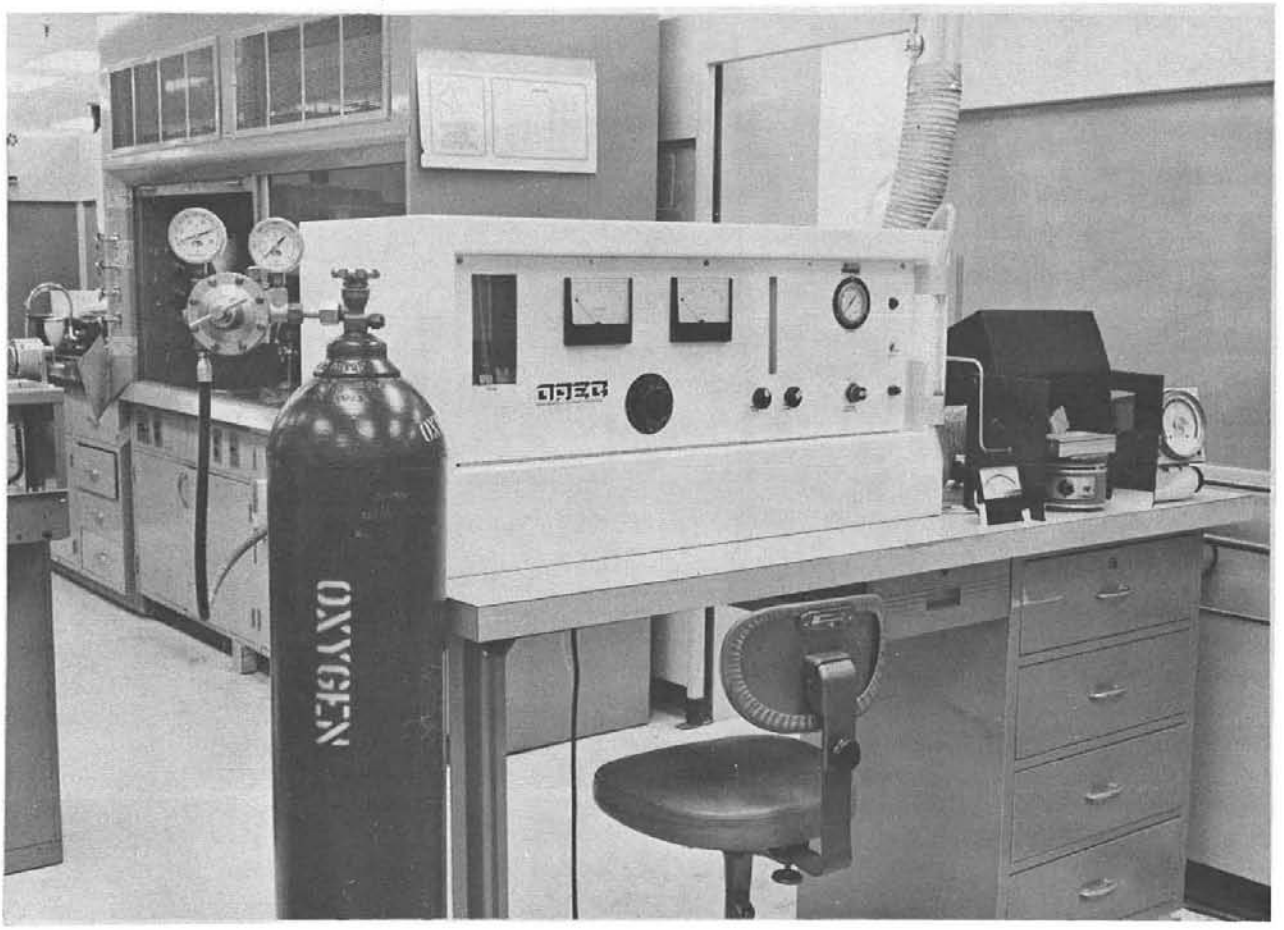


Figure 2. Ozone Generator and Experimental Setup

temperatures. Short wave ultraviolet was generated by a Mineralight lamp, product of Ultra-Violet Products, Inc., San Gabriel, California.

Ozone concentration was maintained at 6 wt% which was determined by titration of sodium thiosulfate in a potassium iodide absorbing solution. The ozone carrier was oxygen gas at a flow rate of 1 liter per minute. The extreme toxicity of ozone is well known and strong exhaust air was used to vent unused ozone to the outside atmosphere. Temperatures used were: $30^{\circ}$, $60^{\circ}$, $90^{\circ}$, $120^{\circ}$, $150^{\circ}$ and $180^{\circ}$C. The three photoresists and the soldering flux that were selected for this study were applied to aluminum oxide ($Al_2O_3$) substrates. Ozone-material reaction time intervals in the ozone chamber were normally from one to two hours depending on the material exposed. The time intervals used were chosen for maximum material removal within the quantity limits on the substrates to provide the most accurate removal rate data. Since it is decomposed flux caused by a soldering operation that normally causes removal problems it was desirable to determine ozone reactivity with flux at its most severely decomposed condition. Initial experimentation with reactivity rates indicated that a mildly activated flux chosen for this experiment was most difficult to remove when decomposed by baking at a temperature of $250^{\circ}$C for 15 minutes. Photoresists were applied and cured in accordance with manufacturer's instructions.

Graphite samples in the shape of discs 2.54 cm in diameter and 1.68 mm thick were made from graphite electrodes. The material was a product of Airco Speer designated as "High Density Extruded Graphite", grade 580, particle size .203 mm. Density was 1.76 gm/cc (2.25gm/cc is theoretical) and the ash level of 1000 ppm consisted of calcium, vanadium, titanium, iron and aluminum. These graphite discs provided relatively consistent exposure areas from sample to sample.

For the gravimetric method of determining material loss subsequent to $O_3$ exposure, weighing was done at the Sandia Laboratories Mechanical Calibration Section on a Mettler, Model M5, microbalance. All samples were allowed to soak in the weighing laboratory environment for 16 hours prior to weighing. Accuracy of weight within operator and equipment capability was $\pm 5$ micrograms.

Table 1 shows day-to-day variation of bare substrate weight. Table 2 shows weight variation from day to day of substrates coated with flux. It was assumed that these variations were because of temperature and humidity changes but there was no way for improvement with existing facilities. However, since weight loss quantities because of $O_3$ reaction were to be in the hundreds of micrograms these

| Substrate Number | | | | |
|---|---|---|---|---|
| Days | 1 | 2 | 3 | 4 |
| 1 | -24 | -24 | -32 | -26 |
| 2 | +36 | +38 | +44 | +32 |
| 3 | +6 | --- | --- | +3 |

Table 1 Weight variation in micrograms from day to day of flux coated substrates

| Substrate Number | | | | |
|---|---|---|---|---|
| Days | 1 | 2 | 3 | 4 |
| 1 | +7 | +4 | | |
| 2 | +21 | +22 | | |
| 3 | +2 | -4 | | |
| 1 | | | +1 | -6 |
| 2 | | | +22 | +8 |

Table 2 Weight variation in micrograms from day to day of bare substrates

variations were considered not significant. References will be made in this report to cleaning per SS289358. This was an internal specification that defined a cleaning procedure for assemblies or parts prior to subsequent bonding or rework operations and consisted of the following sequence of steps:

1 - Boiling trichloroethylene wash
2 - Room temperature alcohol rinse
3 - Boiling detergent wash
4 - Room temperature deionized water rinse
5 - Hot deionized water rinse in cascade washer
6 - Dry nitrogen gas drying

In hybrid microcircuit assembly, as has been indicated previously, thermocompression bonding may be difficult or impossible because of residual contaminants, such as soldering flux, that cannot normally be removed by cleaning solvents. The objective of a portion of this study after establishing the increased efficiency of ozone reaction at 150°C was to determine the time intervals of ozone reaction required to eliminate this problem. Flux and KMER were the selected contaminants since they were the most difficult to remove (Figure 3). Substrates with vacuum deposited gold received typical soldering application and KMER resist application. Solvent cleaning was per SS289358 (outlined previously). Ozone cleaning was applied for intervals of 5, 15 and 30 minutes at a temperature of 150°C. This was done both with and without ultraviolet through the quartz window on the chamber directly incident on the substrates. Thermocompression ball bond testing was done with .025 mm gold wire which is very sensitive to organic surface contamination. In testing, an acceptable bond was indicated when the wire broke in pull testing, the bond remaining intact.

## RESULTS

Figure 3 displays curves showing rates of material removed by ozone at three temperatures. The materials used were Alpha 611 flux, and photoresists: Riston, KMER and AZ1350. It will be noted that flux and KMER resist are relatively unaffected at temperatures below 150°C, and at about 120°C or less actual increases in weight occur. This is possibly due to intermediate oxidative processes such as aldehyde, ketones, and acid group formation. The other two resists, RISTON and AZ1350 exhibit a linear increase in reactivity or weight loss with ozone as temperature is increased. With consideration for minimum thermal degradation of hybrid

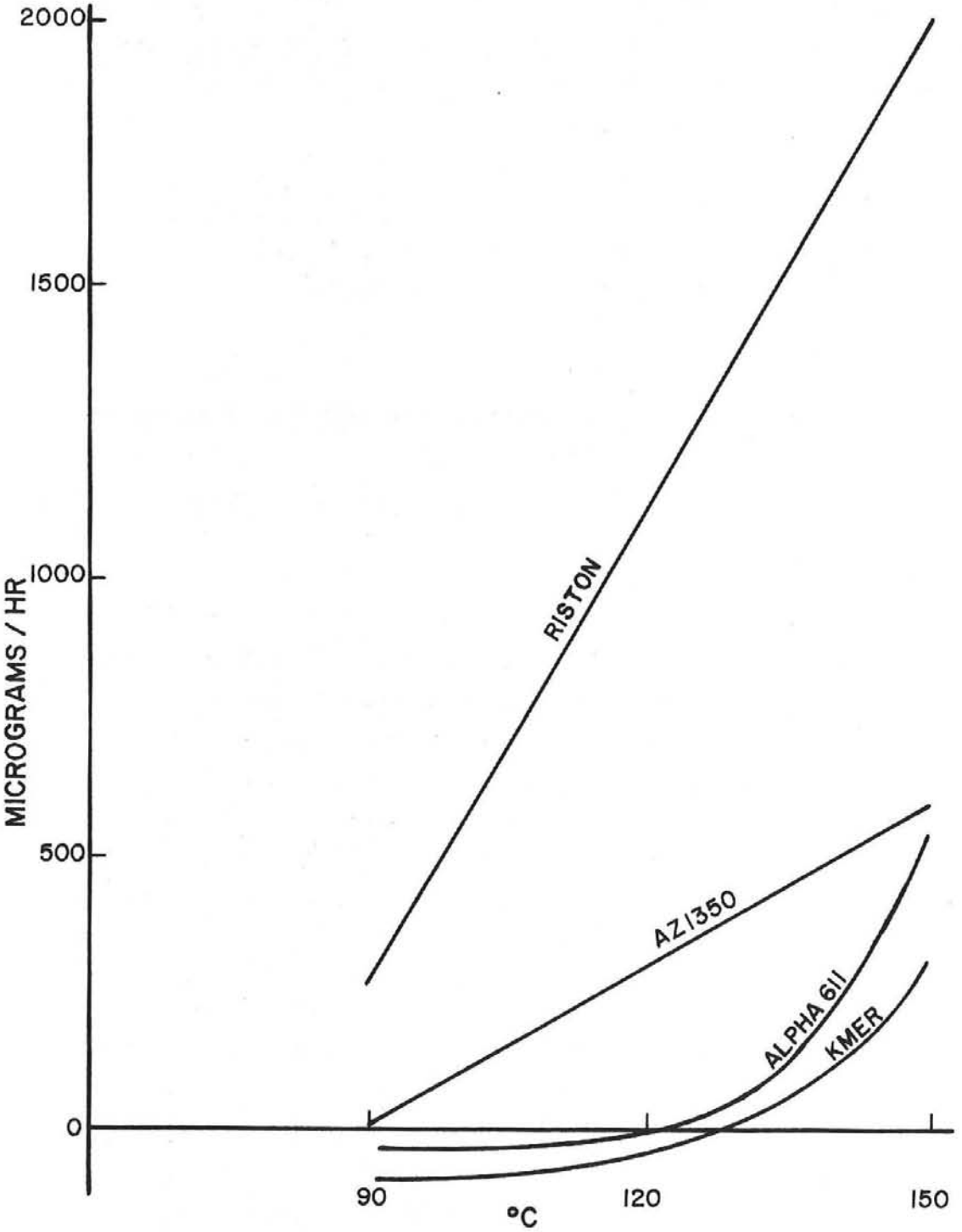


Figure 3. Material Removal Rates Due to Interaction with Ozone at Temperatures Above Ambient

microcircuit structural materials and the desired acceleration of ozone reactivity with the particular contaminants herein discussed, 150°C became the optimum temperature.

Figure 4 illustrates the Activation Energy curve generated by graphite loss data at temperatures from 30°C through 180°C. Activation Energy is the reaction energy required to go from reactants to products. In this case, reactants and products may be represented by the formula:

$$H + C + XO_y \rightarrow HOH + CO + CO_2$$

The reaction in terms of the weight fraction can be represented

$$W_{reac} = W_o e^{-Q/RT}$$

Where Q = Activation Energy, R = Universal gas constant and T = absolute temperature (°K)

then $$\ln W_{reac} = \ln W_o + \ln e^{-Q/RT}$$

and $$\ln W_{reac} = \ln W_o - \frac{1}{T}\left(\frac{Q}{R}\right).$$

The slope of the $\ln W_{reac}$ vs. $\frac{1}{T}$ curve is Q/R. The least squares line fit to the data shown in this Figure 4 has a slope of $8.45 \times 10^3$. Using $R = 1.998 \times 10^{-3}$ kcal/mole - °K, we find Q = 16.8 kcal/mole.

In the residual contamination clean-up experiment, a 5 minute exposure to ozone, at 150°C was observed to be sufficient to yield acceptable thermocompression gold bonds on previously flux (ALPHA 611) contaminated and solvent (SS289358) cleaned surfaces. Five minutes was insufficient for ultraviolet exposure to have significant effect. Clean-up was sufficiently accelerated by the 150°C temperature. KMER resist as removed by solvents (SS289358) did not affect bonding integrity, therefore received no consideration for ozone cleaning. Flux contaminants, however, even after cleaning per SS289358 would not allow acceptable bonding. The 15 minute and 30 minute ozone cleaning runs proved to be excessive, however, obviously also provided good bonding.

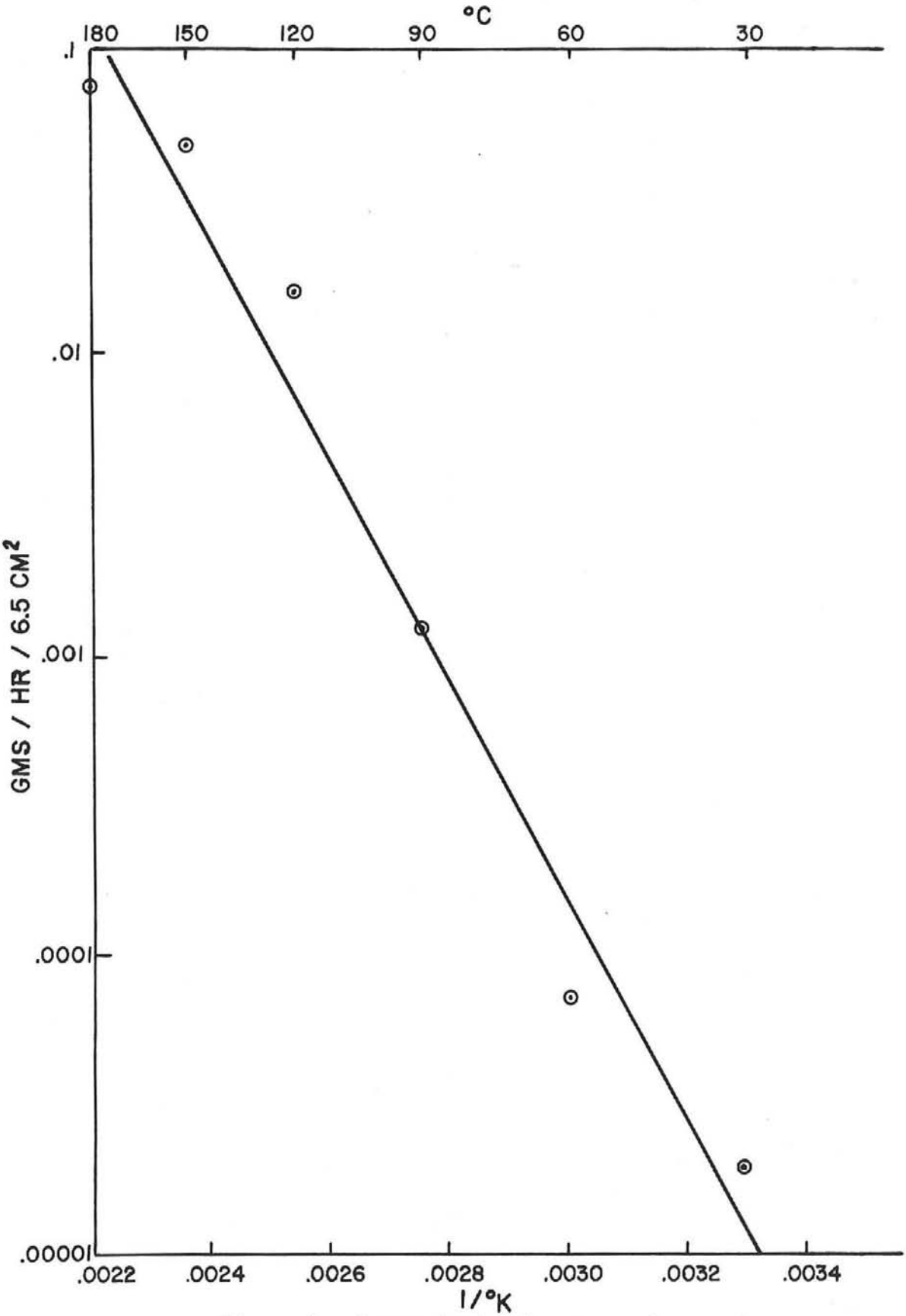


Figure 4. Energy Activation Curve for Graphite

## CONCLUSIONS

Ozone interaction with graphite, and photoresists such as RISTON and AZ1350 was linearly accelerated as the reaction temperature increased. For a commonly used flux (ALPHA 611), and for KMER photoresist, the rate of interaction was increased very little until a temperature of 150°C was realized at which the interaction rate was dramatically increased. On the basis of this work it has been demonstrated that ozone interaction with graphite and organocarbons can be greatly increased by maintaining a temperature of 150°C.

Flux contaminated and solvent cleaned surfaces, that were unbondable by the thermocompression method, were made bondable after a 5-minute ozone clean at 150°C.

Ozone at a concentration of 6 wt% in oxygen and a temperature of 150°C becomes an effective and rapid final stage cleaning agent for the removal of trace amounts of residual flux and photoresists after normal solvent cleaning. The use of graphite in these experiments illustrates that even one of the most stable allotropes or forms of carbon, hence hydrocarbons, are susceptable to oxidative degradation and cleaning in ozone.

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